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Liquidus Curves of $NaNO_3$(*aq*) Calculated from the Modified Adsorption Isotherm Model for Aqueous Electrolytes

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Summary. The *Stokes-Robinson* modification of the *Brunauer-Emmett-Teller* (BET) adsorption isotherm is used to calculate the liquidus curve of $NaNO_3$(*aq*) including the eutectic point and metastable phases. The method described here represents a simplified approach to predict the liquidus curves with sparse information.

Keywords. Activity coefficients; Aqueous electrolytes; *Brunauer-Emmett-Teller*; BET; Adsorption isotherm; Eutectic.

Introduction

In this paper it is demonstrated that the liquidus curve for $NaNO_3$(*aq*) calculated from the *Stokes-Robinson* application of the *Brunauer-Emmett-Teller* adsorption isotherm is in good agreement with experimental data. The water activity equation is obtained from the *Stokes-Robinson*-BET model [1], modified slightly in the algebraic sign of the energy parameter ε, based on the statistical development of the ionic lattice model by *Ally* and *Braunstein* [2]. The solute activities are obtained from the expression derived by *Abraham* [3] with ε defined as mentioned. The values of the two BET parameters are taken as $r = 1.8$ and $\varepsilon = 1.0\,\mathrm{kJ \cdot mol^{-1}}$ and kept fixed in all calculations despite the fact that they exhibit a small temperature dependence [4]. Since the $NaNO_3$(*aq*) system apparently does not possess crystalline hydrates, the approach for calculating the liquidus curve (solid-liquid equilibria) from the general thermodynamic treatment of *Ally* and *Braunstein* [5] is simplified.

Results and Discussion

Solid-liquid equilibria: Ice formation

The chemical potential of ice at a given temperature in equilibrium with its saturated solution is given by $\mu^*_{\mathrm{ice}} = \mu_{\mathrm{w}}$, where μ^*_{ice} is the chemical potential of pure ice (solid) and μ_{w} is the chemical potential of water in the same solution (containing $NaNO_3$). The above equality of chemical potentials is elaborated as

$$\mu^{*}_{\mathrm{ice}} = \mu^{\otimes}_{\mathrm{w}} + \mathrm{R}T \ln a_{\mathrm{w}}(T, p, x_{\mathrm{w}}) \tag{1}$$

where $\mu^{\otimes}_{\mathrm{w}}$ is the chemical potential of pure water at temperature T and one atmosphere pressure, a_{w} is the water activity in $NaNO_3(aq)$, R is the gas constant ($8.314\times10^{-3}\,\mathrm{kJ\cdot mol^{-1}}$), x_{w} is the mole fraction water, and T is the saturation temperature. Differentiating Eq. (1) with respect to T^{-1}, rearranging, and integrating gives

$$R\int_{a_{\mathrm{w}}=1}^{a_{\mathrm{w}}} \mathrm{d}\ln a_{\mathrm{w}} = -\int_{T_{\mathrm{m}}}^{T} (h_{\mathrm{w}}(\mathrm{liquid}) - h^{*}_{\mathrm{ice}})\mathrm{d}\,T^{-1} = -\int_{T_{\mathrm{m}}}^{T} L_{\mathrm{w}}\mathrm{d}\,T^{-1} \tag{2}$$

where $L_{\mathrm{w}} = ((h_{\mathrm{w}}(\mathrm{liquid}) - h^{*}_{\mathrm{ice}})$ is the latent heat of fusion ($6.009\,\mathrm{kJ\cdot mol^{-1}}$) and T_{m} is the melting point (273.15 K) of pure ice [6]. The minor dependence of L_{w} on temperature is ignored. Integration of Eq. (2) and rearrangement gives

$$\ln a_{\mathrm{w}} = \frac{L_{\mathrm{w}}}{\mathrm{R}}\left[\frac{1}{T_{\mathrm{m}}} - \frac{1}{T}\right] \tag{3}$$

The relationship between water activity and water mole fraction in the *Stokes-robinson*-BET model is

$$\frac{M_{\mathrm{w}} m a_{\mathrm{w}}}{1000(1 - a_{\mathrm{w}})} = \frac{1}{cr} + \frac{(c-1)}{cr} a_{\mathrm{w}} \tag{4}$$

where $c = \exp(\varepsilon/\mathrm{R}T)$, m is the molality of $NaNO_3(aq)$, and M_{w} is the molar mass of water at equilibrium conditions.

Solving Eqs. (3) and (4) simultaneously for m yields the equilibrium concentration from which the mole fraction of water, x_{w}, is readily obtained.

Solid-liquid equilibria: $NaNO_3(aq)$ liquidus curve

The chemical potential of anhydrous $NaNO_3$ in equilibrium with its saturated solution at a temperature T can be described by $\mu^{*}_{\mathrm{s}}(x_{\mathrm{s}} = 1, T) = \mu^{\mathrm{solution}}_{\mathrm{s}}(x_{\mathrm{s}}, T)$ where $\mu^{*}_{\mathrm{s}}(x_{\mathrm{s}} = 1, T)$ is the chemical potential of pure anhydrous $NaNO_3$ precipitate and $\mu^{\mathrm{solution}}_{\mathrm{s}}(x_{\mathrm{s}}, T)$ is the chemical potential of $NaNO_3$ in saturated solution at the same temperature. The equality in chemical potentials is written in expanded form as

$$\mu^{*}_{\mathrm{s}}(x_{\mathrm{s}}, T) = \mu^{\mathrm{liq}}_{\mathrm{s}}(x_{\mathrm{s}} = 1, T) + \mathrm{R}T\ln a_{\mathrm{s}}(x_{\mathrm{s}}, T) \tag{5}$$

where $\mu^{\mathrm{liq}}_{\mathrm{s}}(x_{\mathrm{s}} = 1, T)$ is the chemical potential of pure anhydrous liquid (hypothetical) $NaNO_3$ at temperature T and $a_{\mathrm{s}}(x_{\mathrm{s}}, T)$ is the activity of $NaNO_3$ in solution at equilibrium with $NaNO_3$ precipitate at the same temperature. Again, differentiation of Eq. (5) with respect to T^{-1} and integration gives

$$\mathrm{R}\int_{1}^{a_{\mathrm{s}}} \mathrm{d}\ln a_{\mathrm{s}}(x_{\mathrm{s}}, T) = \int_{T_{\mathrm{ms}}}^{T} (h^{\mathrm{solid}}_{\mathrm{s}}(x_{\mathrm{s}} = 1, T) - h^{\mathrm{liquid}}_{\mathrm{s}}(x_{\mathrm{s}} = 1, T))\mathrm{d}T^{-1} = -L_{\mathrm{ms}}\int \mathrm{d}T^{-1} \tag{6}$$

where L_{ms} is the latent heat of fusion ($15.7\,\mathrm{kJ}\cdot\mathrm{mol}^{-1}$) and T_{ms} (583.15 K) the fusion temperature of anhydrous $NaNO_3$ [6]. Completing the integration of Eq. (6) and rearranging gives

$$\ln a_{\mathrm{s}}(x_{\mathrm{s}}, T) = \frac{L_{\mathrm{ms}}}{\mathrm{R}}\left(\frac{1}{T_{\mathrm{ms}}} - \frac{1}{T}\right) \tag{7}$$

The solute activity in the *Stokes-Robinson*-BET model is obtained from *Abraham* [3] and *Ally* and *Braunstein* [5] as

$$\frac{\lambda(1 - x_{\mathrm{s}})}{x_{\mathrm{s}}(1 - \lambda)} = \frac{r}{c} + \frac{r(c-1)\lambda}{c} \tag{8}$$

where $\lambda = a_{\mathrm{s}}^{(1/r)}$, x_{s} is the stoichiometric mole fraction of the salt, and r and ε retain the same identities and values as in Eq. (4). The composition of the liquidus curve is given by x_{s} when Eqs. (7) and (8) are satisfied simultaneously at a given temperature. Metastable liquidus compositions are calculated in the same way by proceeding to temperatures lower than the eutectic point.

It should be noted that since the *Stokes-Robinson*-BET model provides a free energy function which is extensive and homogeneous in the mole numbers; its chemical potentials satisfy the *Gibbs-Duhem* relation automatically [2, 7].

The predicted liquidus curves show good agreement, with experimental data (Fig. 1), especially in the location of the eutectic point. The freezing point depressions are given by the loci of points corresponding to the liquidus curve for water. Agreement with experimental data and the proper location of the eutectic

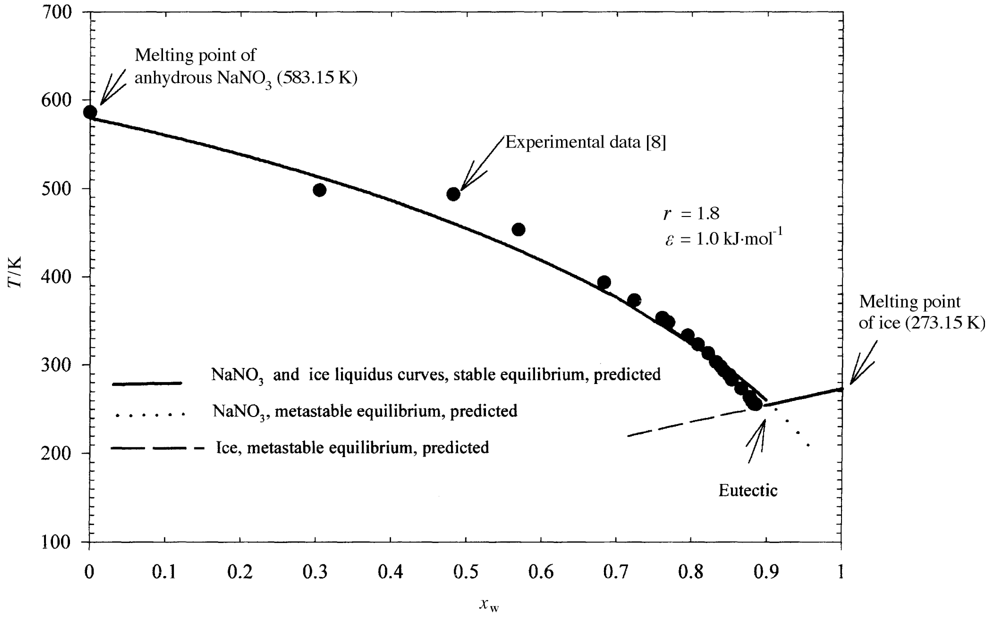

Fig. 1. Liquidus curve from pure water (ice) to pure anhydrous liquid $NaNO_3$(*aq*) at its melting point; comparison of predicted against sparse experimental data [8]

point justifies ignoring the temperature dependence of the enthalpy terms L_{m} and L_{ms}.

The ability of the *Stokes-Robinson* adsorption isotherm to predict the liquidus curve of water in dilute solutions is interesting. *Ally* and *Braunstein* [9] and *Ally* [10] have investigated the concentration regime over which the *Stokes-Robinson* adsorption isotherm applies before showing signs of deterioration. In this regard, the predicted and experimental osmotic coefficients provide a good indicator of the validity of the model [10]. In the dilute solution regime, the excess properties are negligibly small, so even if the model is inaccurate in this region, it does not have a significant bearing on the derived properties, *i.e.* the liquidus curve in this case.

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